Supplementary Information for

More water-soluble brown carbon after the residential "coal-to-gas" conversion measure in urban Beijing

Wei Yuan[1,2], Ru-Jin Huang[1,2,3]*, Jincan Shen[4], Kai Wang[5], Lu Yang[1,2], Ting Wang[1], Yuquan Gong[1,2], Wenjuan Cao[1], Jie Guo[1], Haiyan Ni[1], Jing Duan[1], Thorsten Hoffmann[6]

[1]State Key Laboratory of Loess and Quaternary Geology, Center for Excellence in Quaternary Science and Global Change, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China

[2]University of Chinese Academy of Sciences, Beijing 100049, China

[3]Laoshan Laboratory, Qingdao 266061, China

[4]Key Laboratory of Detection Technology R&D on Food Safety, Food Inspection and Quarantine Technology Center of Shenzhen Customs, Shenzhen 518045, China

[5]Key Laboratory of Plant-Soil Interactions of MOE, College of Resources and Environmental Sciences, National Academy of Agriculture Green Development, China Agricultural University, Beijing 100193, China

[6]Department of Chemistry, Johannes Gutenberg University of Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

***Correspondence**: Ru-Jin Huang (rujin.huang@ieecas.cn)

Supplementary Information consists of 1 note, 2 tables and 15 figures.

Supplementary Note 1

Calculation of average element composition characteristics

The peak abundance-weighted average molecular mass (MMavg), elemental ratios (O/Cavg and H/Cavg), double bond equivalent (DBE_{avg}) and aromaticity equivalent (Xc_{avg}) for the formula CcHhOoNnSs were calculated using following equations.

$$MM_{avg} = \sum(MM_i \times Int_i)/\sum Int_i \quad (1)$$

$$O/C_{avg} = \sum(O/C_i \times Int_i)/\sum Int_i \quad (2)$$

$$H/C_{avg} = \sum(H/C_i \times Int_i)/\sum Int_i \quad (3)$$

$$DBE_{avg} = \sum(DBE_i \times Int_i)/\sum Int_i \quad (4)$$

$$Xc_{avg} = \sum(X_{C_i} \times Int_i)/\sum Int_i \quad (5)$$

Here Int_i is the peak intensity for each individual chromophore *i*.

Supplementary Tables

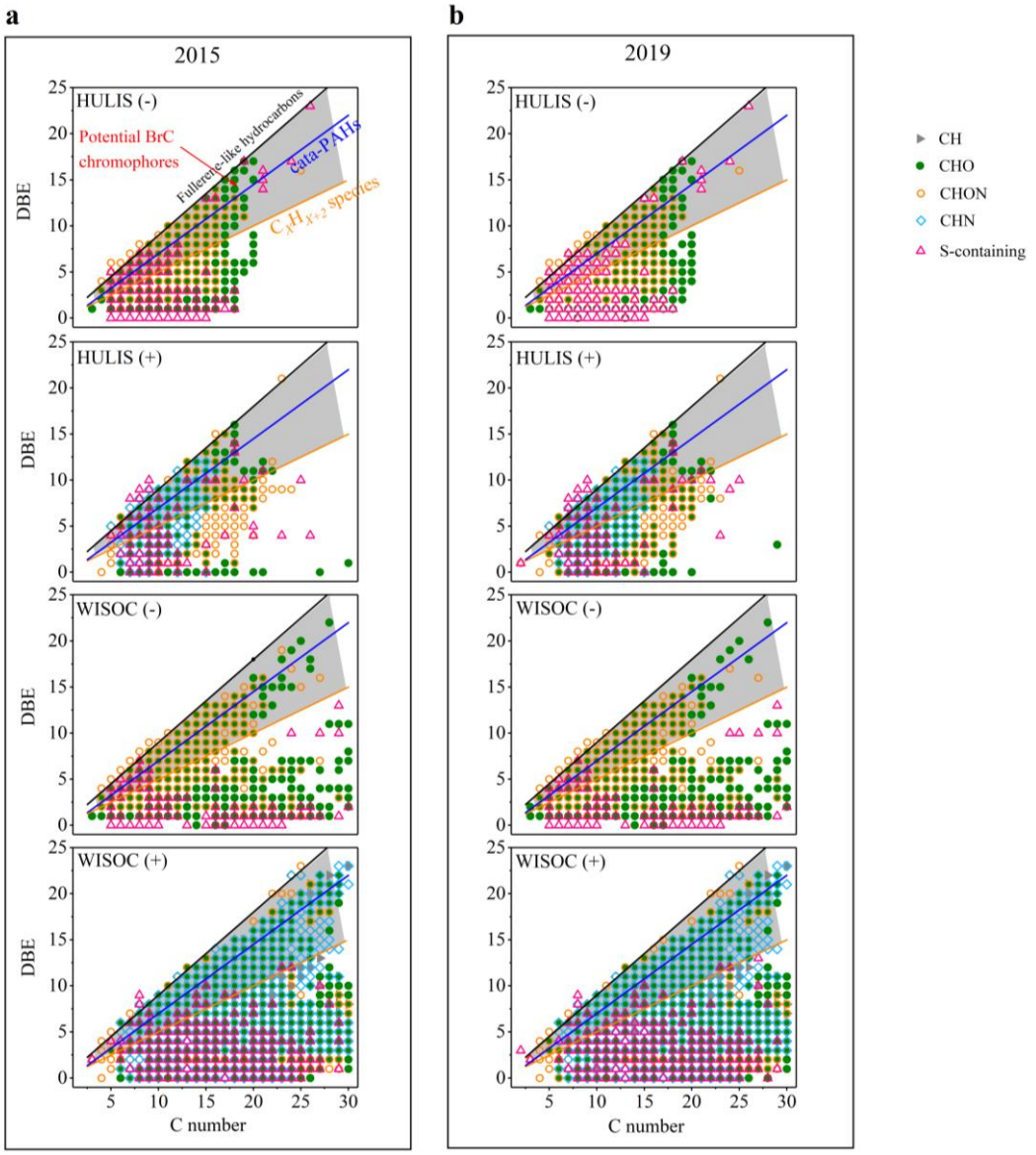
Supplementary Table 1. The peak intensity-weighted average molecular formulas (MF_{avg}), molecular mass (MM_{avg}), elemental ratios, double bond equivalent (DBE_{avg}) and aromaticity equivalent (Xc_{avg}) for chromophores in HULIS-BrC and WI-BrC fractions before (2015) and after (2019) "coal-to-gas" conversion measure.

Samples	Elemental composition	MF_{avg}	MM_{avg}	O/C_{avg}	H/C_{avg}	DBE_{avg}	Xc_{avg}
2015 HULIS-BrC (–)	Total		175.63	0.43	0.89	6.14	2.49
	CHON (–)	$C_{7.67}H_{7.21}O_{3.50}N_{1.11}$	169.82	0.47	0.94	5.62	2.45
	CHO (–)	$C_{9.85}H_{8.21}O_{3.43}$	180.31	0.36	0.84	6.74	2.56
	CHOS (–)	$C_{8.65}H_{7.17}O_{5.04}S_{1.00}$	222.61	0.60	0.84	6.06	2.21
	CHONS (–)	$C_{7.85}H_{7.86}O_{6.16}N_{1.09}S_{1.00}$	246.92	0.82	0.99	5.47	1.73
2019 HULIS-BrC (–)	Total		176.51	0.44	0.88	6.13	2.49
	CHON (–)	$C_{7.62}H_{7.06}O_{3.59}N_{1.18}$	171.45	0.49	0.92	5.67	2.45
	CHO (–)	$C_{9.66}H_{8.05}O_{3.60}$	180.51	0.39	0.84	6.63	2.55
	CHOS (–)	$C_{8.67}H_{7.50}O_{5.22}S_{1.00}$	226.01	0.63	0.88	5.92	2.05
	CHONS (–)	$C_{7.38}H_{6.88}O_{5.77}N_{1.10}S_{1.00}$	234.16	0.84	0.93	5.49	1.76
2015 HULIS-BrC (+)	Total		176.69	0.19	0.86	7.36	2.55
	CHON (+)	$C_{10.21}H_{9.96}O_{1.95}N_{1.30}$	182.95	0.19	0.97	6.88	2.51
	CHO (+)	$C_{10.86}H_{7.98}O_{2.56}$	180.21	0.25	0.74	7.87	2.54
	CHN (+)	$C_{10.03}H_{9.42}N_{1.31}$	149.21	0.00	0.94	6.97	2.71
	CHOS (+)	$C_{11.64}H_{7.00}O_{1.71}S_{1.00}$	207.09	0.20	0.62	9.14	2.48
	CHONS (+)	$C_{9.90}H_{7.64}O_{4.60}N_{2.12}S_{1.00}$	262.74	0.53	0.73	8.14	2.42
2019 HULIS-BrC (+)	Total		179.01	0.22	0.87	7.22	2.49
	CHON (+)	$C_{10.13}H_{10.12}O_{2.24}N_{1.38}$	187.85	0.22	1.0	6.76	2.44
	CHO (+)	$C_{10.56}H_{7.79}O_{2.74}$	179.45	0.27	0.74	7.66	2.48
	CHN (+)	$C_{9.98}H_{9.42}N_{1.40}$	149.81	0.00	0.94	6.97	2.71
	CHOS (+)	$C_{14.29}H_{9.56}O_{1.44}S_{1.00}$	237.14	0.15	0.65	10.51	2.61
	CHONS (+)	$C_{10.71}H_{8.16}O_{4.33}N_{2.20}S_{1.00}$	269.75	0.50	0.71	8.73	2.57
2015 WI-BrC (–)	Total		188.95	0.36	0.90	7.03	2.55
	CHON (–)	$C_{8.80}H_{8.81}O_{3.47}N_{1.10}$	184.35	0.42	1.01	5.94	2.46
	CHO (–)	$C_{11.56}H_{8.81}O_{2.93}$	193.39	0.29	0.78	8.15	2.64
	CHOS (–)	$C_{8.17}H_{7.48}O_{5.49}S_{1.00}$	224.32	0.69	0.91	5.43	1.95
	CHONS (–)	$C_{7.31}H_{6.53}O_{5.37}N_{1.00}S_{1.00}$	225.25	0.76	0.89	5.55	1.79
2019 WI-BrC (–)	Total		187.29	0.38	0.89	6.91	2.54
	CHON (–)	$C_{8.56}H_{8.33}O_{3.62}N_{1.21}$	184.97	0.45	0.98	6.00	2.47
	CHO (–)	$C_{11.09}H_{8.56}O_{3.04}$	189.36	0.31	0.79	7.81	2.62
	CHOS (–)	$C_{7.87}H_{7.30}O_{5.60}S_{1.00}$	222.41	0.73	0.92	5.22	1.85
	CHONS (–)	$C_{6.90}H_{6.03}O_{5.46}N_{1.03}S_{1.00}$	221.55	0.82	0.87	5.40	1.78
2015 WI-BrC (+)	Total		205.87	0.09	0.86	9.36	2.70
	CHON (+)	$C_{13.06}H_{12.14}O_{1.78}N_{1.35}$	217.40	0.15	0.95	8.67	2.62
	CHO (+)	$C_{14.15}H_{9.80}O_{2.04}$	213.32	0.16	0.69	10.25	2.70
	CHN (+)	$C_{13.21}H_{11.81}N_{1.42}$	191.33	0.00	0.93	9.01	2.75
	CH (+)	$C_{15.87}H_{13.41}$	204.99	0.00	0.88	10.17	2.78
	CHOS (+)	$C_{12.05}H_{11.42}O_{1.98}S_{1.00}$	220.74	0.24	0.84	7.34	2.36
	CHONS (+)	$C_{13.10}H_{15.51}O_{4.83}N_{2.05}S_{1.00}$	311.71	0.39	1.19	7.37	2.49
2019 WI-BrC (+)	Total		204.05	0.11	0.89	8.94	2.66
	CHON (+)	$C_{12.52}H_{12.12}O_{1.95}N_{1.44}$	214.89	0.17	0.99	8.18	2.57
	CHO (+)	$C_{14.04}H_{9.54}O_{2.21}$	214.45	0.18	0.68	10.27	2.67
	CHN (+)	$C_{12.36}H_{12.03}N_{1.64}$	184.36	0.00	1.02	8.16	2.72
	CH (+)	$C_{16.16}H_{13.19}$	208.18	0.00	0.85	10.56	2.79
	CHOS (+)	$C_{7.00}H_{4.00}O_{3.00}S_{1.00}$	169.00	0.43	0.57	6.00	2.00
	CHONS (+)	$C_{14.91}H_{17.39}O_{5.11}N_{2.07}S_{1.00}$	340.22	0.37	1.17	8.25	2.59

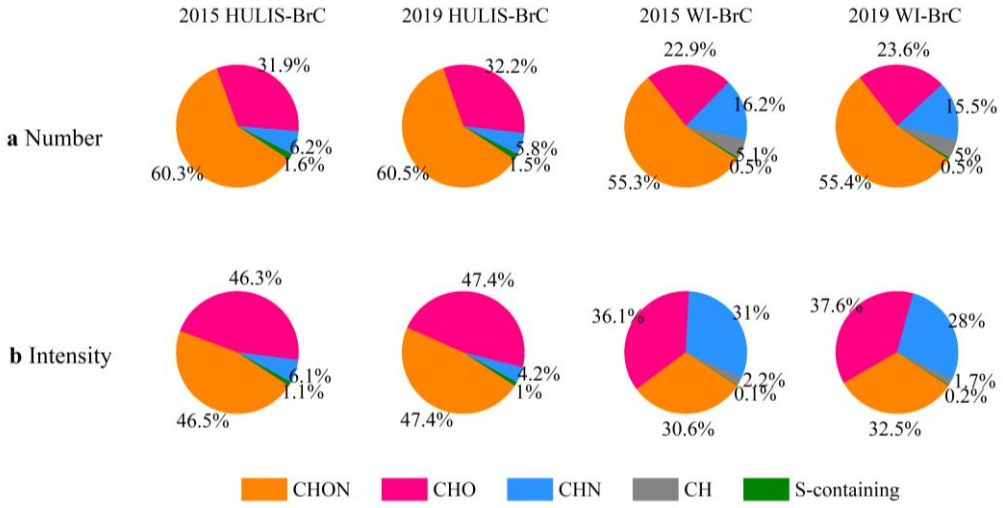
Supplementary Table 2. The light absorption coefficient at 365 nm (Abs_{365}) and organic carbon (OC) concentration of selected samples in this study.

	sample					
2015	1	2	3	4	5	6
Abs_{365} (M m^{-1})	24.3	31.2	40.0	42.7	45.0	47.9
OC (μg m^{-3})	19.7	22.9	23.9	27.1	32.4	33.0
2019	7	8	9	10	11	12
Abs_{365} (M m^{-1})	10.6	12.1	15.6	16.6	21.7	24.7
OC (μg m^{-3})	15.0	12.7	18.2	15.4	18.2	21.9

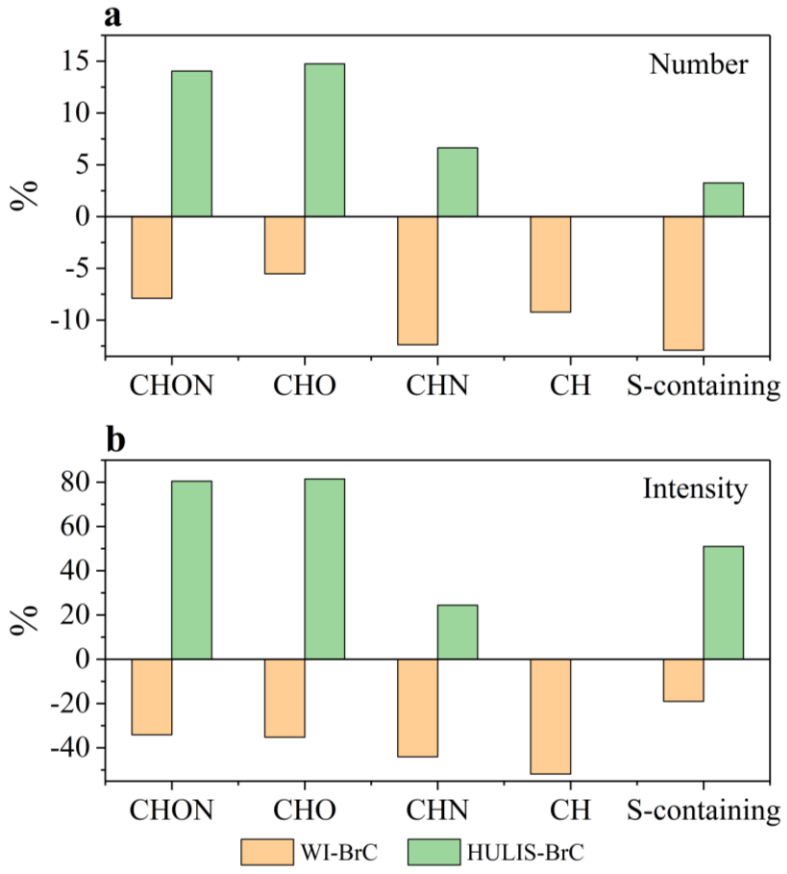
Supplementary Figures



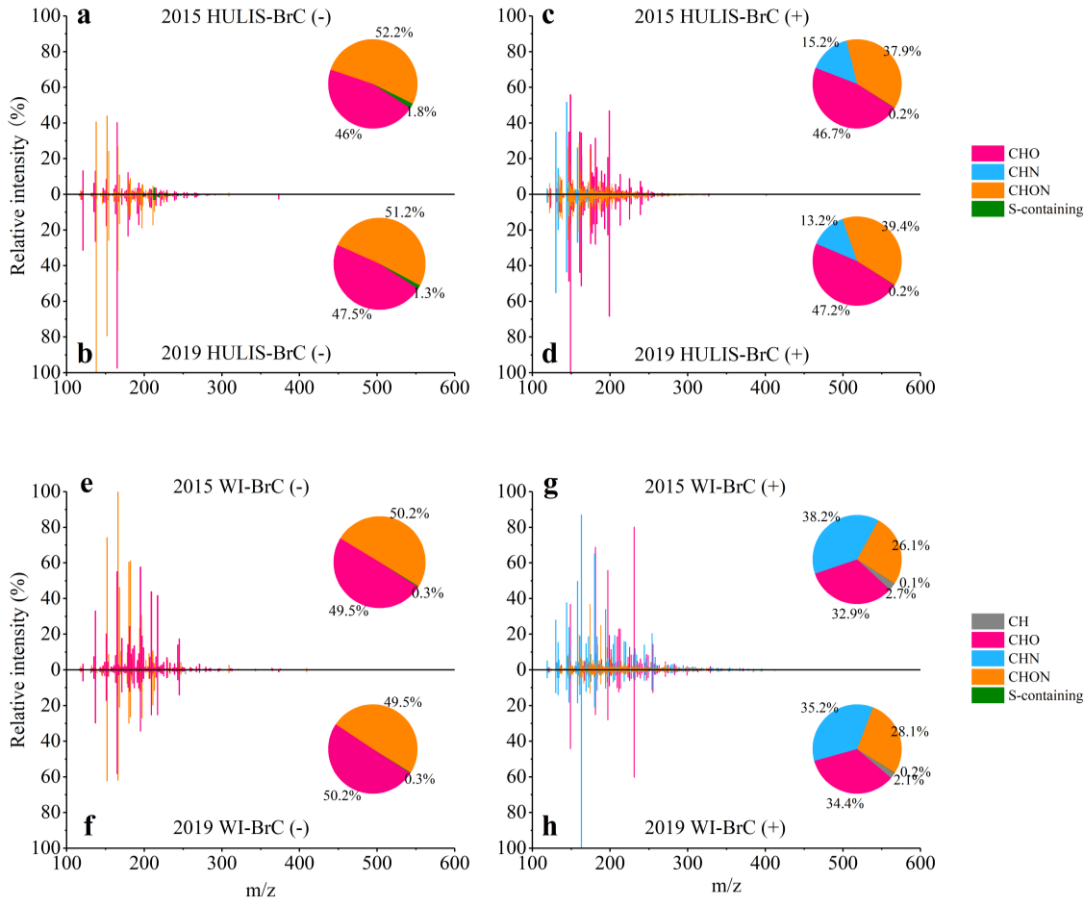
Supplementary Figure 1. Plot of the double bond equivalent (DBE) vs number of carbon atoms in identified compounds in HULIS and WISOC fractions. Compounds identified **a** before (2015) and **b** after (2019) the "coal-to-gas" conversion measure. Lines indicate DBE reference values of linear conjugated polyenes CxHx+2 (yellow solid line), *cata*-condensed PAHs (blue solid line) and fullerene-like hydrocarbons with DBE=0.9*C (gray solid line). Data points inside the gray shaded area are potential BrC chromophores.



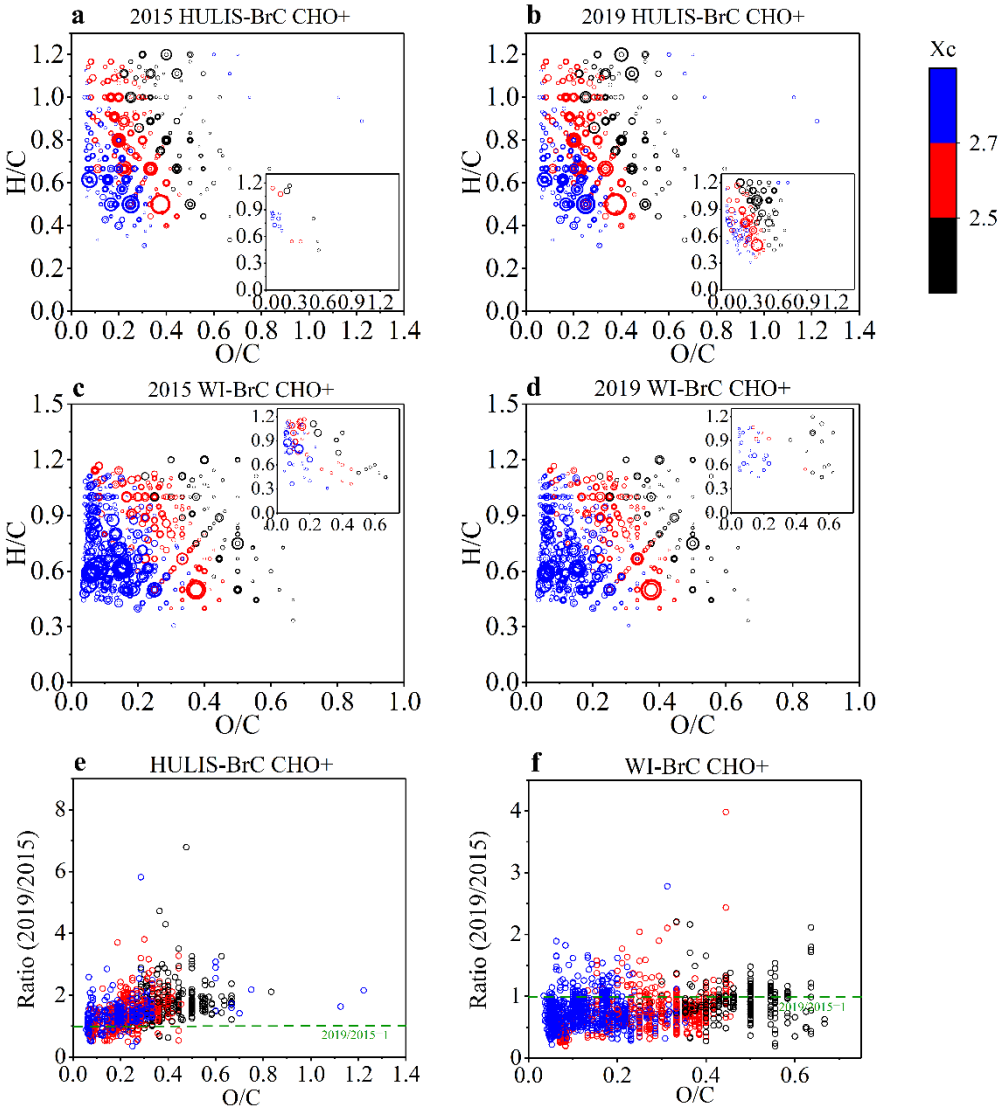
Supplementary Figure 2. Proportions of chromophores in each compound category in HULIS-BrC and WI-BrC fractions before (2015) and after (2019) "coal-to-gas" conversion measure. Proportions of **a** number and **b** intensity.



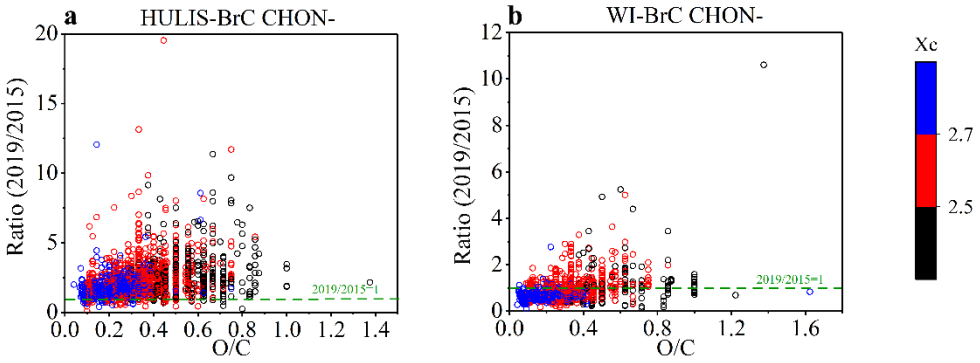
Supplementary Figure 3. Changes ((2019-2015)/2015) of different compound categories in HULIS-BrC and WI-BrC fractions after "coal-to-gas" conversion measure. Changes in **a** number and **b** intensity.



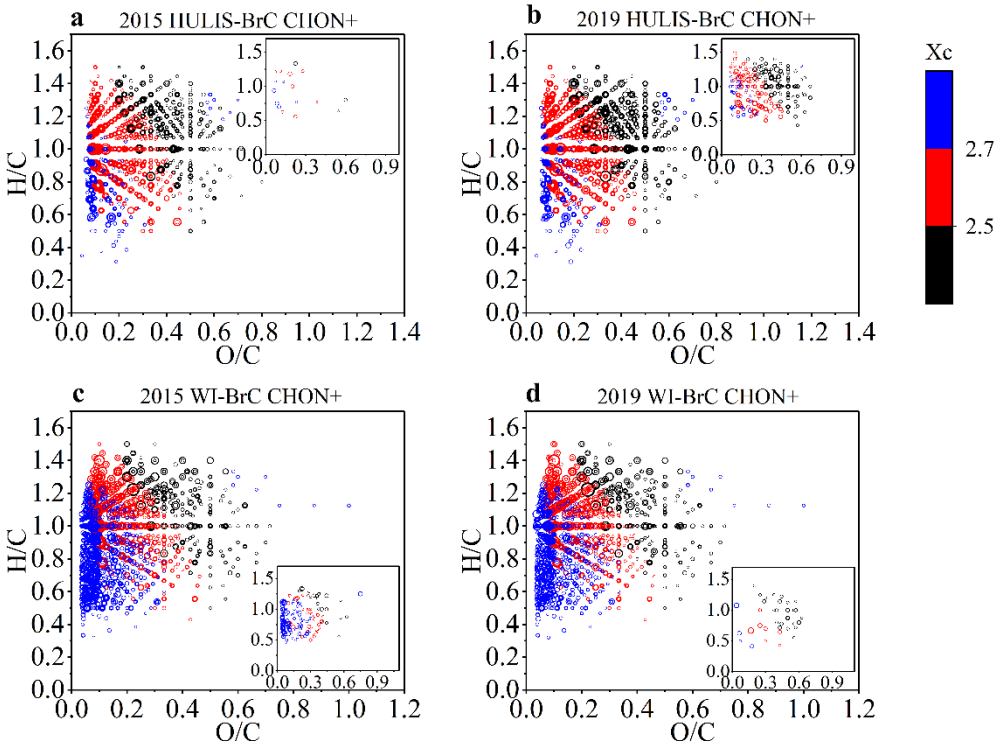
Supplementary Figure 4. Mass spectra of CHO, CHON, CHN, CH, and S-containing chromophore categories before (2015) and after (2019) the "coal-to-gas" conversion measure. Chromophores identified in **a**, **b** HULIS-BrC (-), **c**, **d** HULIS-BrC (+), **e**, **f** WI-BrC (-) and **g**, **h** WI-BrC (+). The pie charts showed the relative intensities of different chromophore categories.



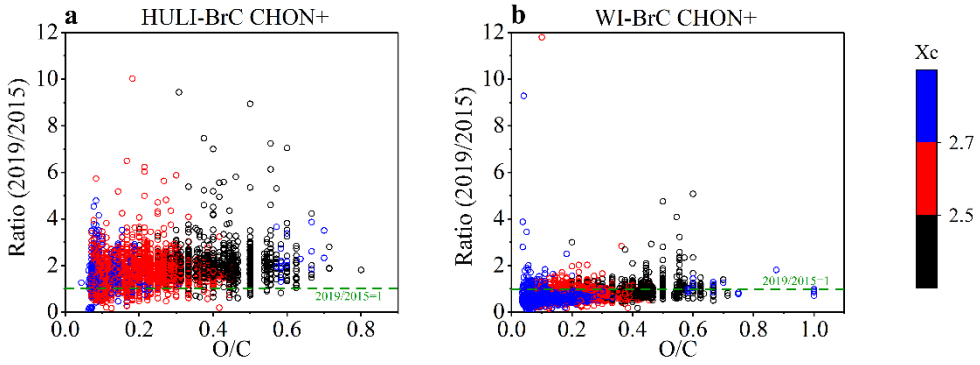
Supplementary Figure 5. Characteristics of CHO+ chromophores before (2015) and after (2019) the "coal-to-gas" conversion measure. a, **b** Van Krevelen diagram for CHO+ chromophores in HULIS-BrC fraction. **c**, **d** Similar to (**a**, **b**), but in WI-BrC fraction. **e** Corresponding intensity ratios of after/before (2019/2015) the measure of CHO+ chromophores in HULIS-BrC fraction. **f** Similar to (**e**), but in WI-BrC fraction. The area of the circles is proportional to the fourth root of the intensity of individual chromophores and the color bar denotes the aromaticity equivalent (black with Xc < 2.5, red with 2.5 ≤ Xc < 2.7, and blue with Xc ≥ 2.7). The insert plot represents the chromophores identified only before or after the measure.



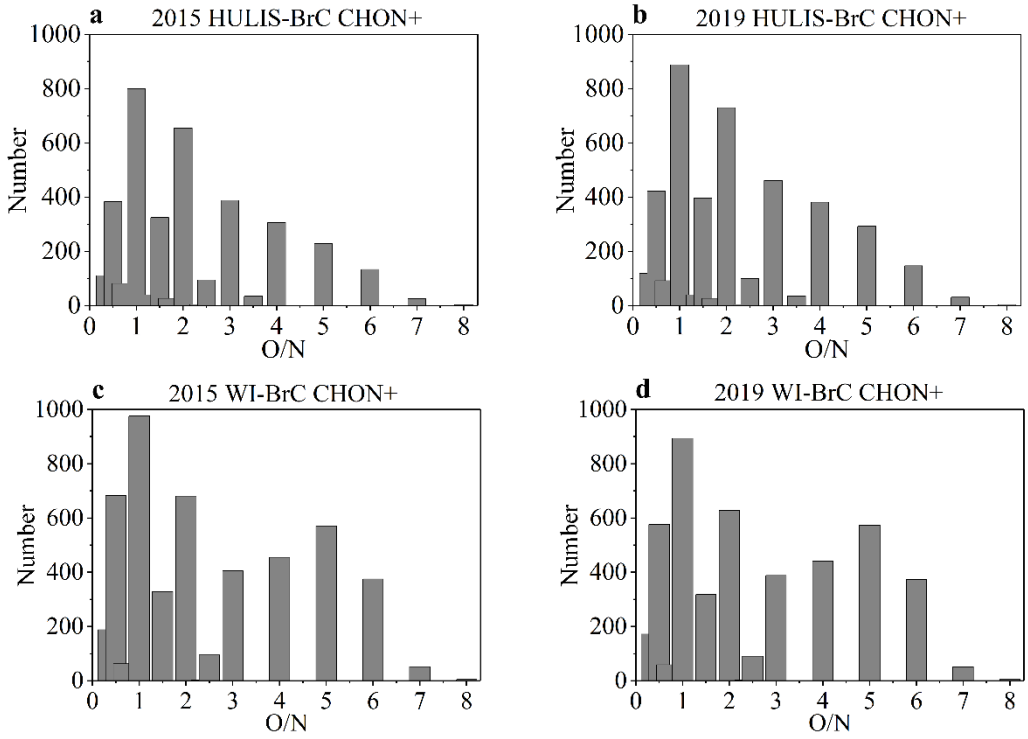
Supplementary Figure 6. Corresponding intensity ratios of after/before (2019/2015) the "coal-to-gas" conversion measure of CHON- chromophores. Intensity ratios in **a** HULIS-BrC and **b** WI-BrC fractions.



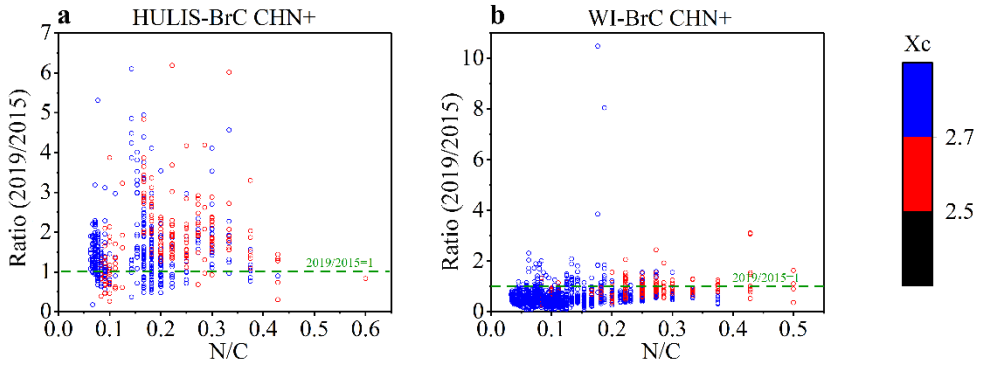
Supplementary Figure 7. Van Krevelen diagram for CHON+ chromophores before (2015) and after (2019) the "coal-to-gas" conversion measure. a, **b** CHON+ chromophores in HULIS-BrC fraction. **c**, **d** CHON+ chromophores in WI-BrC fraction. The area of the circles is proportional to the fourth root of the intensity of individual chromophores and the color bar denotes the aromaticity equivalent (black with Xc < 2.5, red with 2.5 ≤ Xc < 2.7, and blue with Xc ≥ 2.7). The insert plot represents the chromophores identified only before or after the measure.



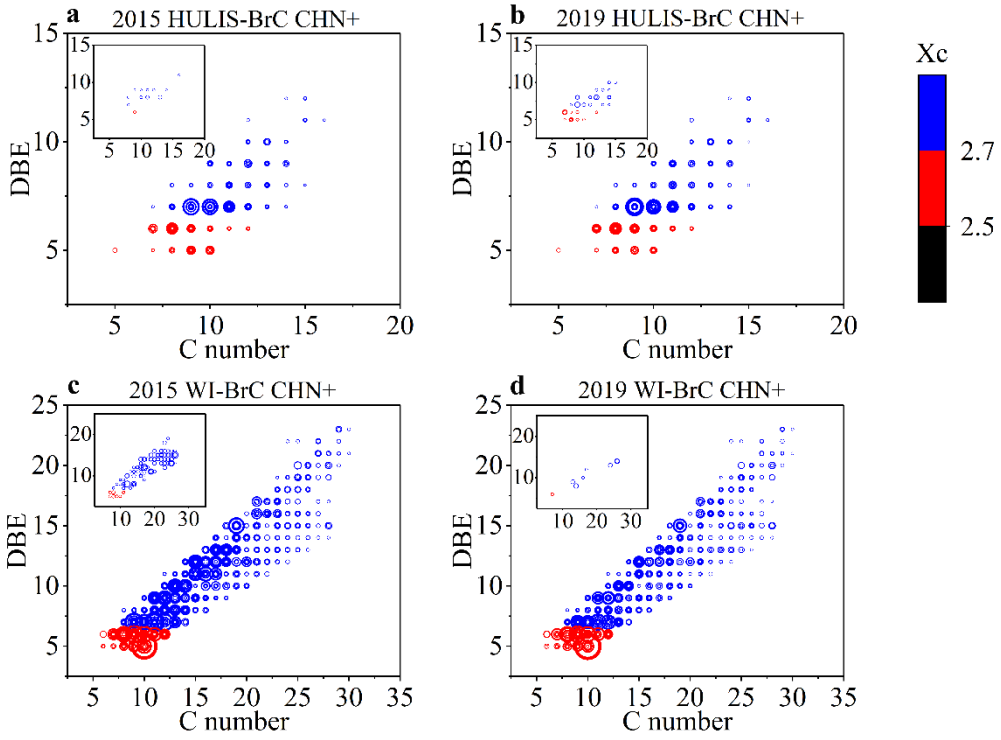
Supplementary Figure 8. Corresponding intensity ratios of after/before (2019/2015) the "coal-to-gas" conversion measure of CHON+ chromophores. Intensity ratios in **a** HULIS-BrC and **b** WI-BrC fractions.



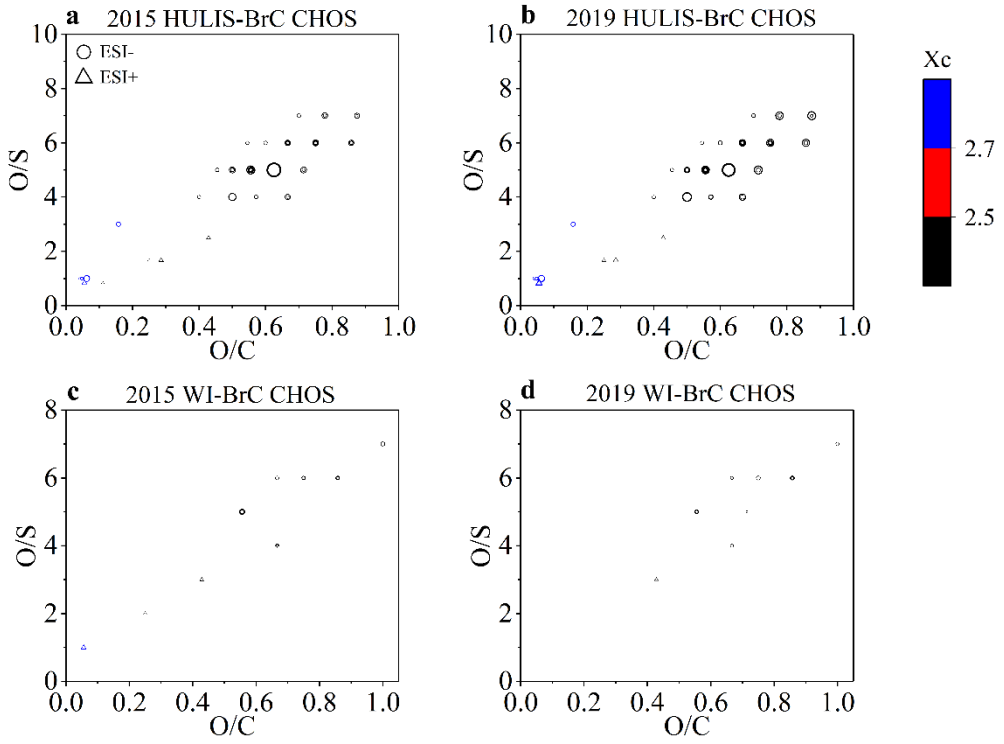
Supplementary Figure 9. Number of different CHON+ chromophores subgroups classified according to O/N ratios in their formulas in HULIS-BrC and WI-BrC fractions. a, **c** Before (2015) the "coal-to-gas" conversion measure. **b**, **d** After (2019) the "coal-to-gas" conversion measure.



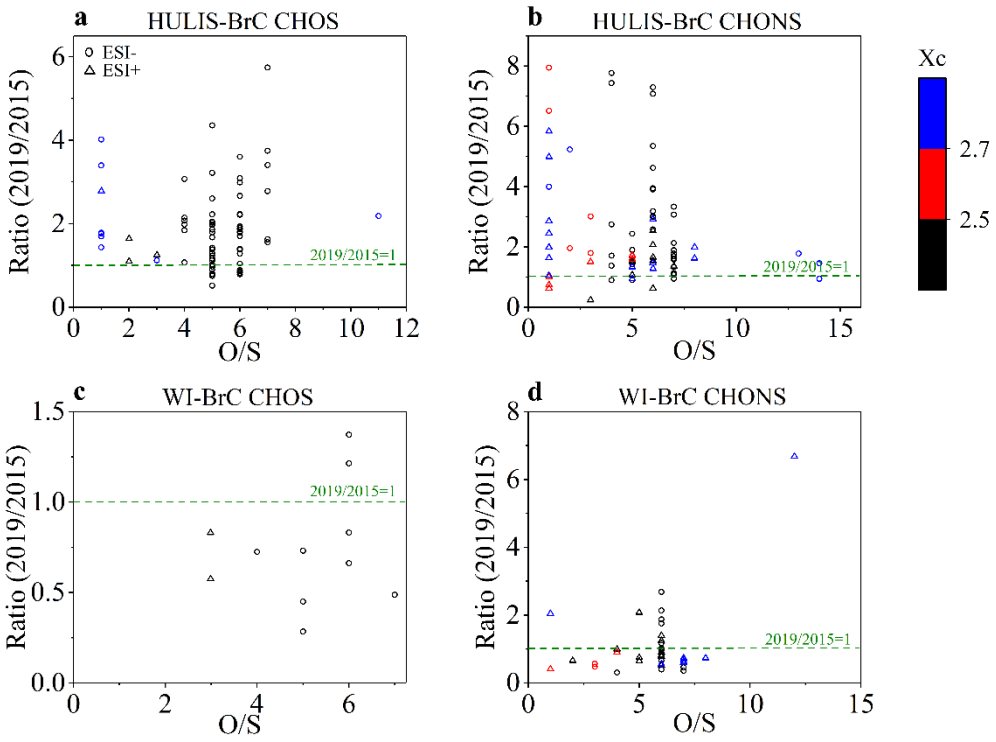
Supplementary Figure 10. Corresponding intensity ratios of after/before (2019/2015) the "coal-to-gas" conversion measure of CHN+ chromophores. Intensity ratios in **a** HULIS-BrC and **b** WI-BrC fractions.



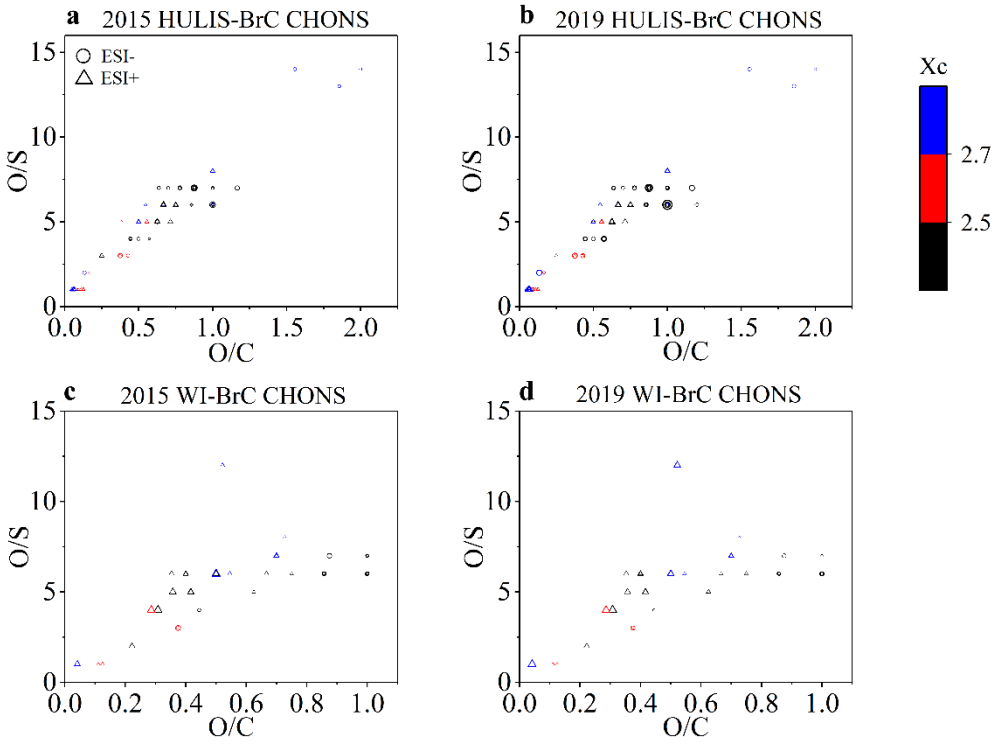
Supplementary Figure 11. Characteristics of CHN+ chromophores before (2015) and after (2019) the "coal-to-gas" conversion measure. Plot of the double bond equivalent (DBE) vs number of carbon atoms in identified CHN+ chromophores in **a**, **b** HULIS-BrC and **b**, **d** WI-BrC fractions. The area of the circles is proportional to the fourth root of the intensity of individual chromophores and the color bar denotes the aromaticity equivalent (black with Xc < 2.5, red with 2.5 ≤ Xc < 2.7, and blue with Xc ≥ 2.7). The insert plot represents the chromophores identified only before or after the measure.



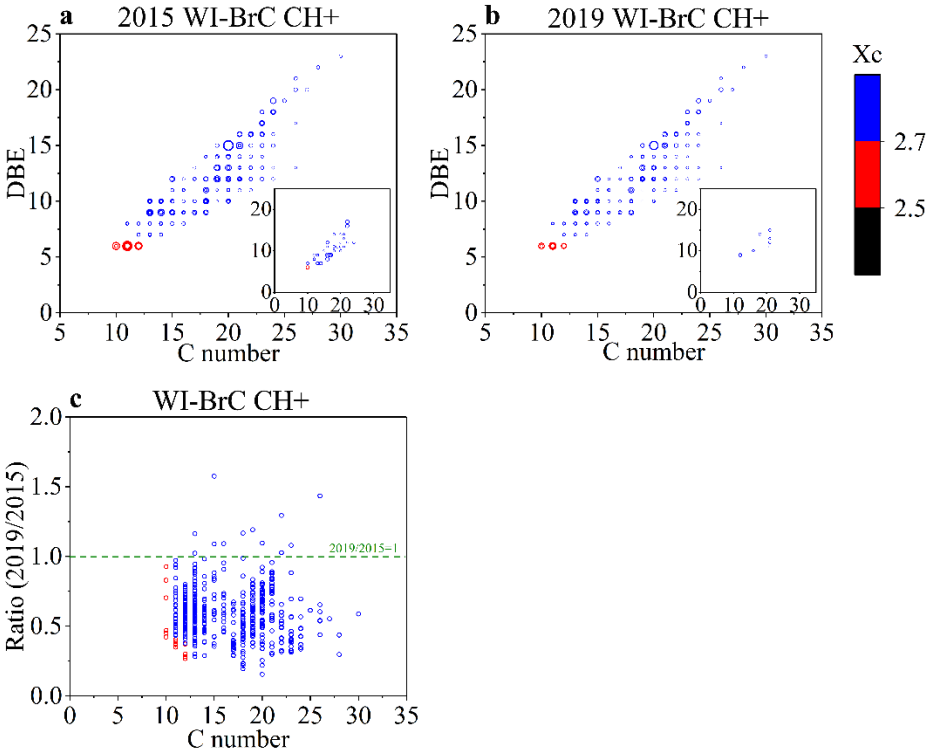
Supplementary Figure 12. Van Krevelen diagram for CHOS chromophores assigned in HULIS-BrC and WI-BrC fractions. a, **c** Before (2015) the "coal-to-gas" conversion measure. **b**, **d** After (2019) the "coal-to-gas" conversion measure. The area of the circles is proportional to the fourth root of the intensity of individual chromophores and the color bar denotes the aromaticity equivalent (black with Xc < 2.5, red with 2.5 ≤ Xc < 2.7, and blue with Xc ≥ 2.7).



Supplementary Figure 13. Corresponding intensity ratios of after/before (2019/2015) the "coal-to-gas" conversion measure of S-containing chromophores in HULIS-BrC and WI-BrC fractions. Intensity ratios of **a**, **c** CHOS and **b**, **d** CHONS chromophores.



Supplementary Figure 14. Van Krevelen diagram for CHONS chromophores before (2015) and after (2019) the "coal-to-gas" conversion measure. CHONS chromophores in **a**, **b** HULIS-BrC and **c**, **d** WI-BrC fractions. The area of the circles is proportional to the fourth root of the intensity of individual chromophores and the color bar denotes the aromaticity equivalent (black with Xc < 2.5, red with 2.5 ≤ Xc < 2.7, and blue with Xc ≥ 2.7).



Supplementary Figure 15. Characteristics of CH+ chromophores in WI-BrC fraction. a Plot of the double bond equivalent (DBE) vs number of carbon atoms in identified CH+ chromophores before (2015) the "coal-to-gas" conversion measure. **b** Similar to (**a**), but after (2019) the "coal-to-gas" conversion measure. **c** Corresponding intensity ratios of after/before (2019/2015) the measure of CH+ chromophores. The area of the circles in a and b is proportional to the fourth root of the intensity of individual chromophores and the color bar denotes the aromaticity equivalent (black with Xc < 2.5, red with 2.5 ≤ Xc < 2.7, and blue with Xc ≥ 2.7). The insert plot represents the chromophores identified only before or after the measure.